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Solution calorimetry of organic nonelectrolytes as a tool for investigation of intermolecular interactions

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Abstract

The paper is mainly the review and generalization of the previous publications of the authors. It demonstrates that solution calorimetry method gives the opportunities of more detailed understanding of various aspects of intermolecular interactions in solution. We are assured that prerequisite to such an understanding is the successive analysis of various solute-solvent systems from the simplest ones which include alkanes as a solute or as a solvent to the most complex systems with solvent self-association via hydrogen bonding. Particular findings discussed in this paper are (i) an inconspicuous contribution of electrostatic solute-solvent interaction to the solvation enthalpy and, accordingly, the dominating contribution of dispersion interactions for nonspecifically solvated solutes; (ii) new, very general method for the extraction of specific interaction enthalpy from the enthalpy of solvation; (iii) new method of determination of self-association enthalpies for the solvents associated via hydrogen bonding; (iv) new method for determination of cooperative hydrogen bonding enthalpies of proton acceptors with associated species of alcohols; (v) the unique method of experimental determination of the hydrophobic effect enthalpy. Copyright © 2007 John Wiley & Sons, Ltd.

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Keywords

Aliphatic alcohols, Cooperativity effect, Enthalpy of solution, Hydrogen bonds, Intermolecular interactions, Linear solvation-energy relationships, Solution calorimetry